



## Project Summary

# Development and Testing of a Surrogate Species Chemical Reaction Mechanism

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**During the first year of a two-year program, a photochemical reaction mechanism was updated and extensively evaluated. The testing and refinement of this surrogate species mechanism was performed in order to create an improved chemical mechanism for the atmospheric simulation models that are used to develop ozone control strategies.**

**The updated mechanism was tested against over 400 environmental chamber experiments carried out in four different chambers. Tests were performed to assess the accuracy of the chamber characterization procedures, of reactions for single organic compounds, and of the overall mechanism for complex organic mixtures, including mixtures obtained from automobile exhaust. The results indicate the mechanism's predictions are generally consistent with the experimental data.**

***This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in two separate volumes of the same title (see Project Report ordering information at back).***

### Introduction

Atmospheric simulation models are essential planning tools for the development of emission control strategies for regions that presently exceed the ambient air quality standard for ozone. The models are used to estimate the emissions control requirements needed to prevent exceedances of the air quality

standards in the future. One of the most important components in atmospheric simulation models is the chemical mechanism that describes the formation of ozone from volatile organic compounds (VOC) and oxides of nitrogen ( $\text{NO}_x$ ). As part of a coordinated research program to develop reliable ozone control strategies, the U.S. Environmental Protection Agency (EPA) sponsored this research study to develop and test an improved chemical mechanism.

Many chemical mechanisms have been developed in the last ten years for simulating ozone formation from VOC and  $\text{NO}_x$ . All of the mechanisms intended for atmospheric applications incorporate approximations and condensations of species and reactions because it is currently impossible to explicitly include reactions for the hundreds of organic compounds present in ambient air. Several approaches are available for lumping the organic species into a manageable number of chemical classes in the mechanisms. The approach adopted in this study was to use the surrogate species approximation where the explicit chemistry of selected compounds is used to represent the chemistry of all similar compounds. For example, the explicit reactions for propene and trans-2-butene are used as surrogates for the reactions of terminally double-bonded and internally double-bonded alkenes. Provided the mechanism is formulated with a sufficient number of surrogate species (10 or more), the surrogate species approach is quite capable of representing the majority of organic species present in urban air.

The surrogate species approach has several advantages over other schemes such as the carbon bond lumping approach. Surrogate species mechanisms can easily be updated and expanded since the reactions for each surrogate species are independent of other parts of the mechanism. Also, since whole molecules rather than lumped bond groups are used in the surrogate species mechanisms, they are not reliant on the assumption that different parts of the molecules react independently.

Prior to this study, surrogate species chemical mechanisms had been subjected to only limited testing against environmental chamber data. A key purpose of this research program was to extensively test the predictive ability of an updated surrogate species mechanism against chamber data for a broad range of conditions.

## Formulation of the Chemical Mechanism

The mechanism of Atkinson et al.\* was extensively updated and expanded to incorporate the most recent kinetic and mechanistic data obtained in laboratory studies. The new mechanism includes reactions for the following species:

- **Inorganic:** The reactions of the inorganic species NO, NO<sub>2</sub>, O<sub>3</sub>, CO, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>2</sub>, HONO<sub>2</sub>, HO<sub>2</sub>NO<sub>2</sub>, OH, HO<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> are represented explicitly.
- **Alkanes:** A lumped alkane species "C<sub>4</sub>-C<sub>5</sub>" is used to represent the reactions of the C<sub>4</sub> and C<sub>5</sub> alkanes. The reactions of the C<sub>6</sub> and higher alkanes are represented using a "lumped reaction" approach which represents the net effect of all C<sub>6</sub><sup>+</sup> alkane reactions. Ethane and propane are assumed to be unreactive.
- **Alkenes:** The reactions of the alkenes ethene, propene, and trans-2-butene are represented explicitly. Other terminal olefins are treated as propene; other internal olefins are represented as trans-2-butene.
- **Aromatics:** The initial reactions of the aromatics benzene, toluene, m-xylene, and 1,3,5-trimethylbenzene are represented explicitly. The details of the ring-opening processes, and the subsequent reactions of many of the ring-opened products

are not known, and these are represented by parameterized, semi-empirical mechanisms, with the photolysis rates of the uncharacterized products adjusted to fit the environmental chamber data.

- **Photooxidation Products:** The reactions of the photooxidation products formaldehyde, acetaldehyde, propionaldehyde, acetone, methyl ethyl ketone, 3-pentanol, glyoxal, methylglyoxal, biacetyl, peroxyacetyl nitrate, peroxypropionyl nitrate, and peroxybenzoyl nitrate and the reactions of OH radicals with benzaldehyde and NO<sub>3</sub> radicals with phenolic compounds are represented explicitly. The photolysis of benzaldehyde, the reactions of OH radicals with phenolics, and the reactions of the uncharacterized aromatic ring-opening products are represented by parameterized mechanisms with parameters in some cases adjusted to fit the chamber data.

This updated mechanism incorporates the significant improvements in our understanding of atmospheric reaction mechanisms which have occurred in recent years. Despite these improvements, a number of important uncertainties remain, with two of the most important areas being in the aromatic photooxidation mechanisms and the reactions of ozone with the higher alkenes. These uncertainties necessitate the continued use of parameterization in certain aspects of the mechanism, as indicated above.

## Testing of the New Mechanism

The new chemical mechanism was tested against the data from over 400 experiments. The experiments were carried out in four different environmental chambers: the University of North Carolina's (UNC) 150,000-1 dual outdoor chamber, the Statewide Air Pollution Research Center's (SAPRC) 5800-1 evacuable indoor chamber (EC), the SAPRC's 6400-1 indoor Teflon chamber (ITC), and the SAPRC's 50,000-1 outdoor Teflon chamber (OTC). Procedures were developed to represent the light intensities and spectral distributions of the light sources in the different chambers. Appropriate methods were also developed to characterize the major chamber effects, such as NO<sub>x</sub> off-gassing, ozone deposition and the chamber free radical sources, in a consistent manner for all four chambers.

The testing of the chemical mecha-

nism was carried out without any run-to-run adjustment of uncertain parameters to optimize the quality of fits of the model predictions to the experimental results. While such adjustment would obviously yield better fits, it was not appropriate for the mechanism testing program since it could mask possible systematic errors in the chemistry.

The types and number of environmental chamber experiments used in the testing program are summarized in Table 1. The NO<sub>x</sub>-air, CO-NO<sub>x</sub>-air, n-butane-NO<sub>x</sub>-air and background air experiments were used to test and refine the chamber characterization procedures. Single organic compound-NO<sub>x</sub>-air experiments were employed to test the reactions for each of the organic precursor species included in the mechanism. Experiments with organic mixtures were used to test the predictive ability of the mechanism for conditions representative of the real atmosphere. These ranged from simple mixtures like propene/n-butane to complex mixtures including more than 15 compounds and automobile exhaust.

In general, the performance of the mechanism in simulating the results of the 415 experiments modeled was reasonably good considering the current state of knowledge of chamber effects and the NO<sub>x</sub>-air photooxidation mechanisms of organic compounds. Although a number of experiments were not well simulated, and certain systematic discrepancies were observed in the simulations of some groups of experiments, the major features of the majority of the experiments were reasonably well simulated. Most of the discrepancies observed were of a random nature, suggesting that these may be due primarily to chamber-dependent parameters which vary from run to run, rather than systematic errors in the chemical mechanism. The simulations of the outdoor chamber experiments had greater variability in the quality of the fits than the simulations of the indoor experiments; this is consistent with the greater variability of conditions associated with outdoor chamber experiments.

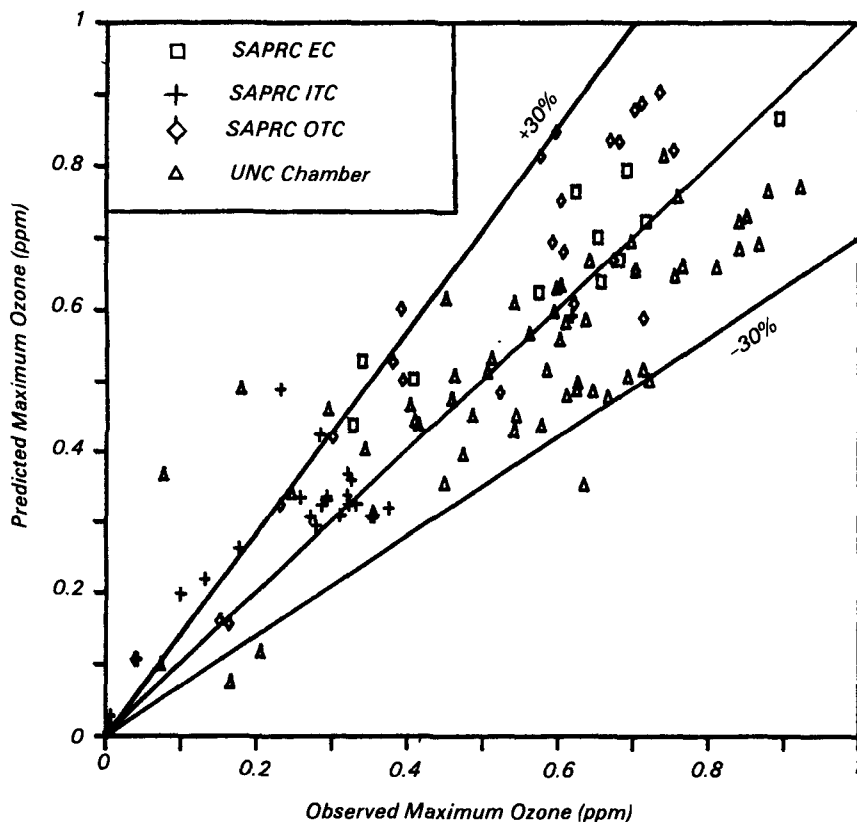
The accuracy of the mechanism's predictions for complex mixtures of organics and NO<sub>x</sub> is most important for its use in atmospheric simulation models and control strategy development. The predictions for maximum ozone concentrations in 117 cases with complex alkane-alkene-aromatic mixtures are compared to the observed values in Figure 1. These results show that the mechanism

\*Atkinson, R., A.C. Lloyd, and K. Winges. 1982. *Atmos. Environ.* 16 (6): 1341-1355.

**Table 1.** Summary of Environmental Chamber Runs Used for Chemical Mechanism Testing

Types of Runs	Number of Runs*			
	UNC	EC	ITC	OTC
Background air, NO <sub>x</sub> -air, Tracer-NO <sub>x</sub> , and CO-NO <sub>x</sub>	27	7	5	5
HCHO-air and HCHO-NO <sub>x</sub>	13	7	1	2
Acetaldehyde-air and Acetaldehyde-NO <sub>x</sub>	9	3	2	6
Propionaldehyde, Methyl ethyl ketone, and Acetone-NO <sub>x</sub>	5			
<i>o</i> -Cresol-NO <sub>x</sub>		1		
Ethene-NO <sub>x</sub>	6	6		
Propene-NO <sub>x</sub>	22	15	3	5
Dynamic propene-NO <sub>x</sub>	5			
1-Butene-NO <sub>x</sub>	4	3		
trans-2-Butene-NO <sub>x</sub>	1	3		
Isobutene-NO <sub>x</sub>			1	
<i>n</i> -Butane-NO <sub>x</sub>	7	14	3	1
C <sub>5</sub> <sup>+</sup> Alkane-NO <sub>x</sub>	6	6	8	
Benzene-NO <sub>x</sub>			6	
Toluene-NO <sub>x</sub>	5	13	2	
<i>m</i> -Xylene-NO <sub>x</sub>		4	2	
<i>o</i> -Xylene-NO <sub>x</sub>	4			
1,3,5-Trimethylbenzene-NO <sub>x</sub>		3	5	
2-, 3- and 4-Component runs, no aromatics	15	15		
2- and 3-Component runs, with aromatics	9	7		
Dynamic propene- <i>n</i> -butane-toluene-NO <sub>x</sub>	4			
Complex multi-component runs	25	11	25	25
Auto exhaust runs	23			
<b>Totals</b>	<b>190</b>	<b>118</b>	<b>63</b>	<b>44</b>
<i>(Grand Total = 415 runs)</i>				

\*UNC = UNC outdoor chamber, EC = SAPRC evacuable indoor chamber, ITC = SAPRC indoor Teflon chamber, OTC = SAPRC outdoor Teflon chamber.



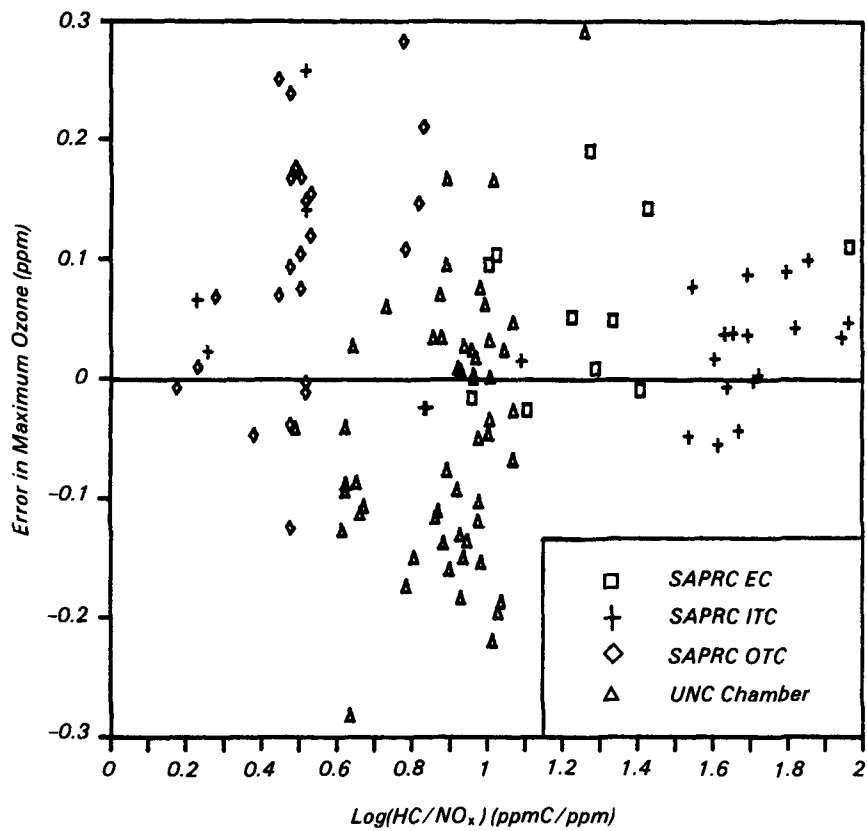
**Figure 1.** Comparison of predicted and observed maximum ozone concentrations for irradiations of complex organic mixtures and NO<sub>x</sub>.

predicts the observed ozone maxima within  $\pm 30\%$  in about 90% of the cases. On the average for these cases, the mechanism overpredicts the ozone maxima by 4%, or 0.02 ppm. The average error is  $\pm 18\%$ , or  $\pm 0.088$  ppm. These predictions are considered quite good. The distribution of the error in maximum ozone predictions with respect to the initial ratio of VOC to NO<sub>x</sub> is shown in Figure 2 for these same cases. The scattered nature of the distribution shows that there are no systematic dependencies of the error on this important ratio, as should be the case for a mechanism that will be applied for a wide range of atmospheric conditions.

### Conclusions

The Atkinson et al. surrogate species chemical mechanism has been updated to reflect the current state of chemical knowledge. It has been tested over a broad range of conditions and has been shown to provide predictions that are generally consistent with the data. The generally high level of performance in simulating complex organic mixtures suggests that the mechanism is suitable for use in atmospheric simulation models.

A second phase of this research program is being carried out to adapt the chemical mechanism for use in atmospheric simulation models. The mechanism will be modified slightly so that it is suitable for use in EPA's Empirical Kinetic Modeling Approach (EKMA). Also a version of the mechanism with fewer reactions and species will be developed for use in multi-cell airshed simulation models.



**Figure 2.** Error in the predicted maximum ozone concentration as a function of  $\log_{10}(\text{HC}/\text{NO}_x)$  for irradiations of organic mixtures and  $\text{NO}_x$ .

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***Marcia Dodge** is the EPA Project Officer (see below).*

*The complete report consists of two volumes, entitled "Development and Testing of a Surrogate Species Chemical Reaction Mechanism:"*

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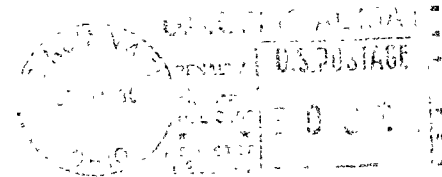
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